Investigation of four Cd(II) sulfonate complexes: crystal structure, Hirshfeld surface analysis, thermogravimetric and spectroscopic properties

Xueyuan Wang, [a] Eduardo Carrillo-Aravena, [b] Yuandong Wu, *[a] Dajiang Mei, [a] Shaoguo Wen [a] and Thomas Doert [b]

* *Dr. Yuandong Wu*

Fax: +86-21-67791214

E-mail: wuyuandong@sues.edu.cn

[a] *College of Chemistry and Chemical Engineering, Shanghai University of Engineering Science, Longteng Road 333, 201620, Shanghai, P.R China.*

[b] *Faculty of Chemistry and Food Chemistry, Technische Universität Dresden, 01062, Dresden, Germany.*

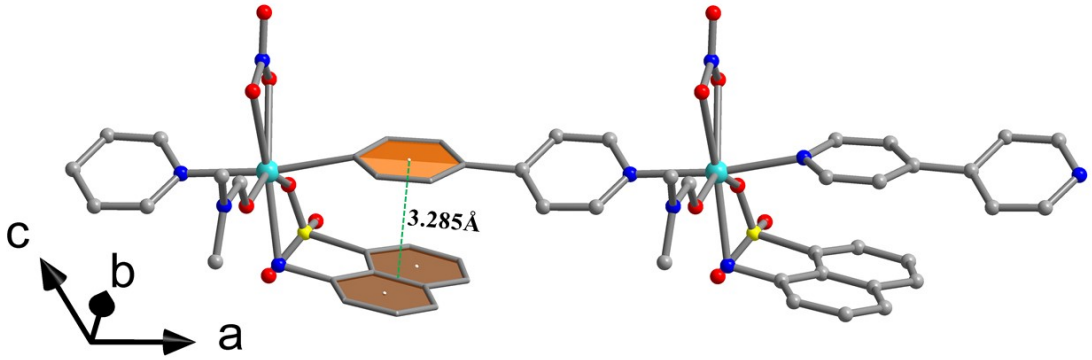

Fig. S1 π-π stacking interactions in complex **2**.

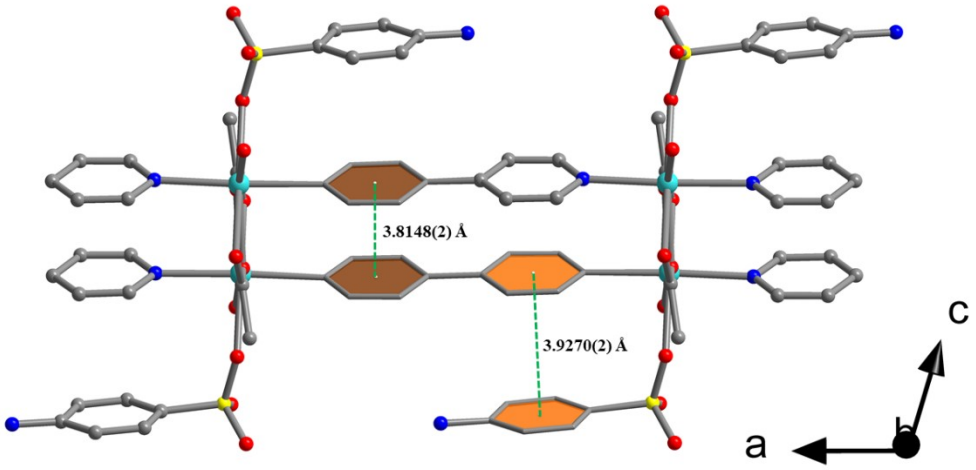

Fig. S2 π-π stacking interactions in complex **3**.

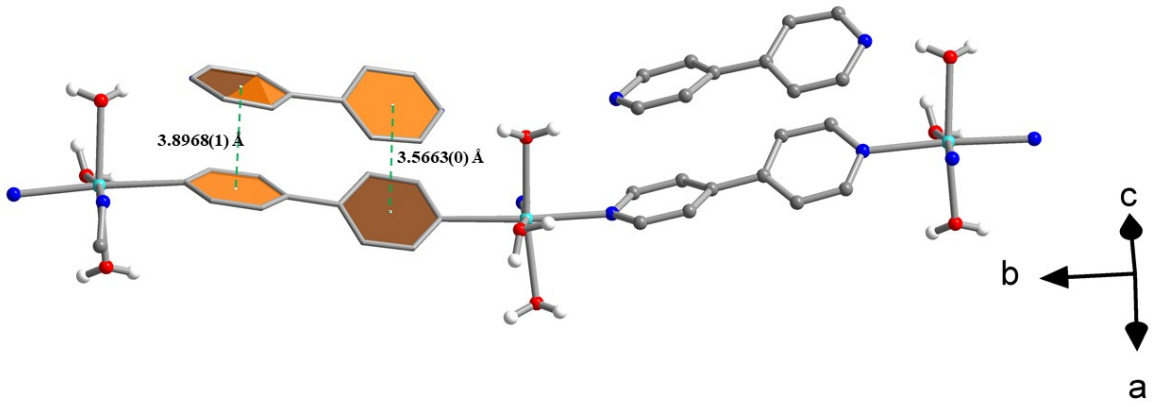

Fig. S3 π-π stacking interactions in complex **4**.

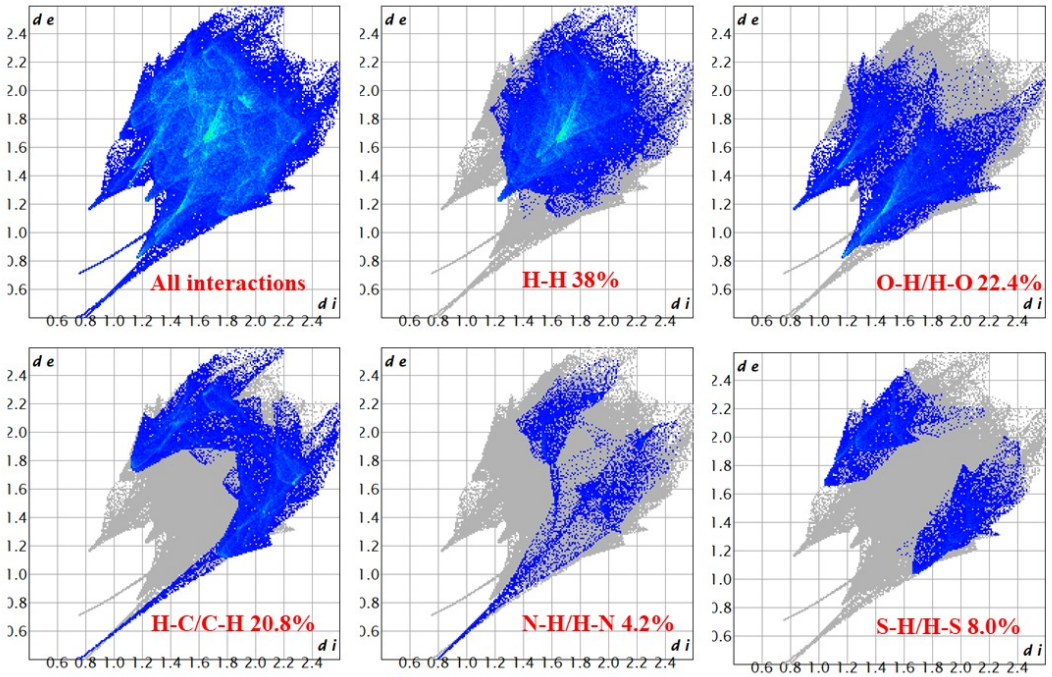

Fig. S4 2D fingerprint plots for Hirshfeld surface of complex **1**.

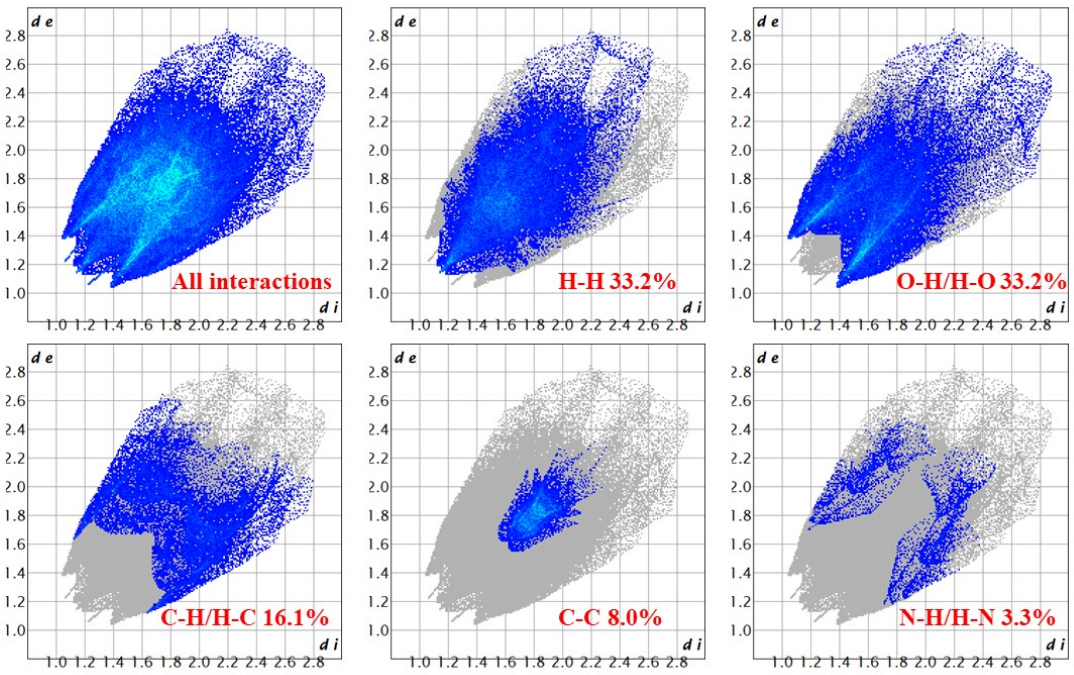

Fig. S5 2D fingerprint plots for Hirshfeld surface of complex **2**.

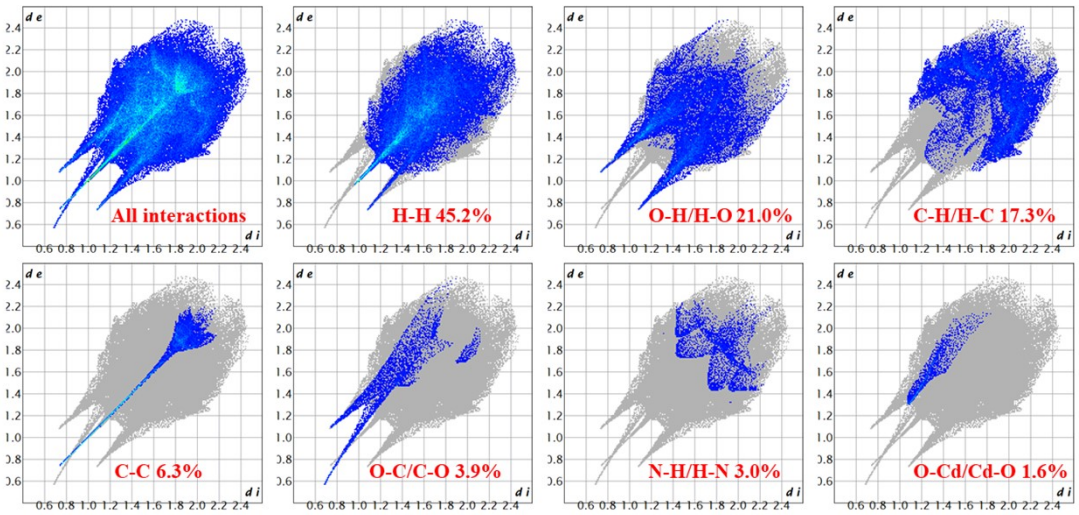

Fig. S6 2D fingerprint plots for Hirshfeld surface of complex **3**.

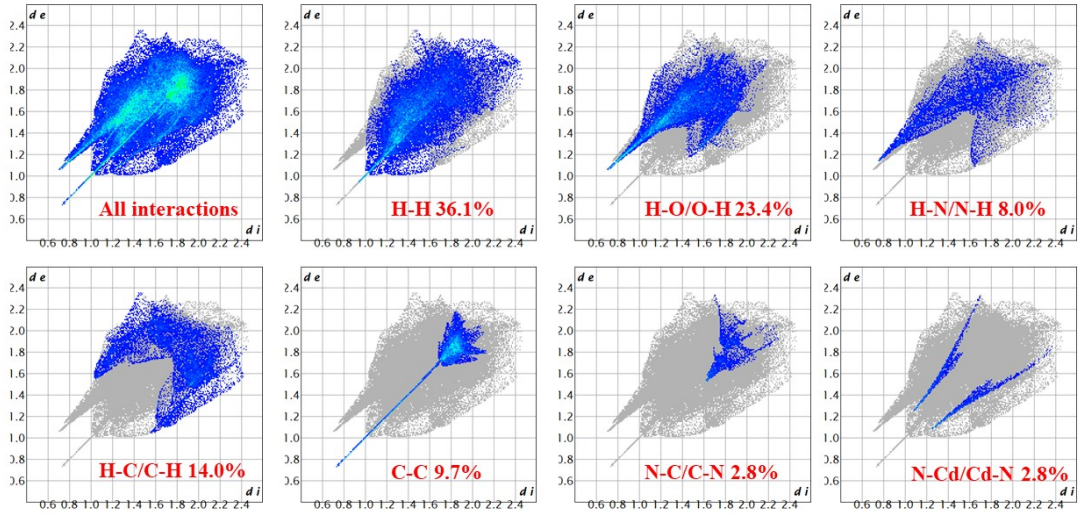

Fig. S7 2D fingerprint plots for Hirshfeld surface of complex **4**.

Powder X-ray Diffraction

The obtained powder samples were analyzed at room temperature on a DX-2700 X-ray diffractometer (Cu Kα, λ=1.54184 Å) with a scanning angle range of 2θ = 5-60˚, the scanning step was 0.02˚. And Mercury software was used to simulate the powder X-ray spectrum of the compound based on the data obtained from single-crystal X-ray diffraction. The positions of the diffraction peaks in the experimentally obtained spectra and those in the simulated spectra are basically consistent as shown in Fig. S8, indicating that the compounds are pure phases. And the difference in diffraction intensity is mainly caused by the different orientations preferred by the powder samples in collecting diffraction data.

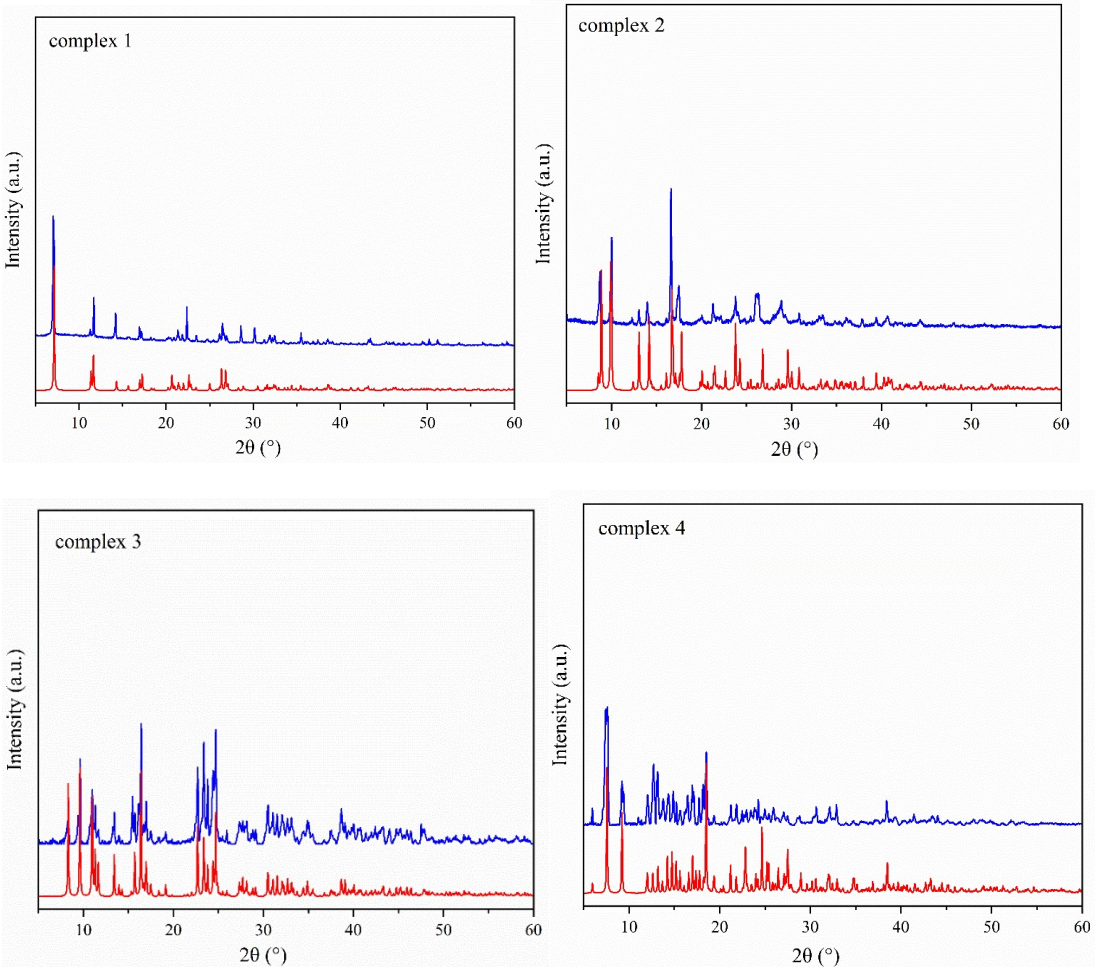

Fig. S8 Powder X-ray diffraction patterns of complexes **1-4.**

IR spectroscopy:

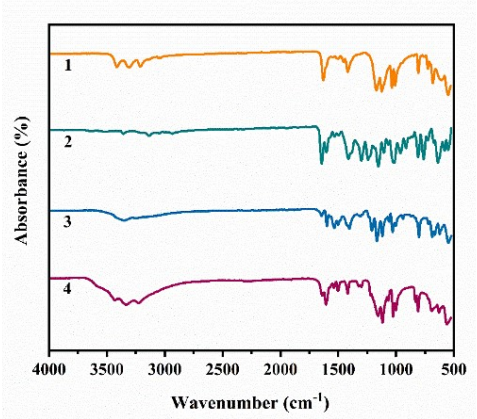

Fig. S9 IR spectroscopy of complexes **1-4.**

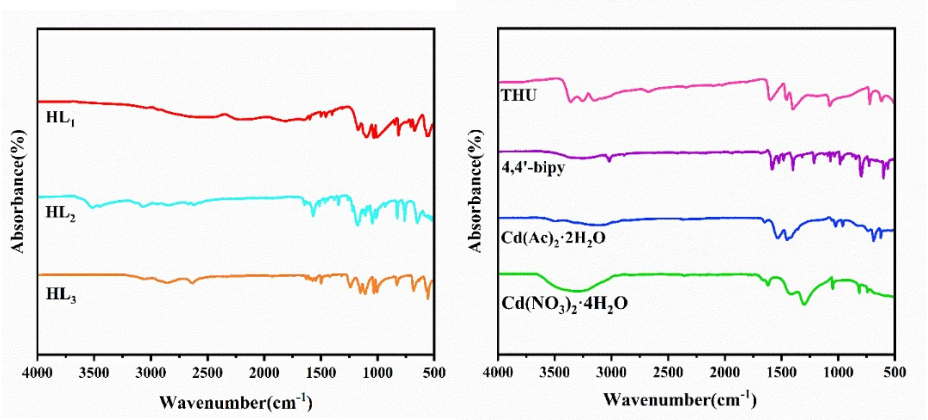

Fig. S10 IR spectroscopy of free ligands.

Table. S1 Assignments for ligands:

Assignments	Frequencies /cm^{-1}				
	HL_1	HL_2	HL_3	4,4'-bipy	THU
$\nu_{N—H/O-H}$	3031	3512, 3440, 3058	3062, 3044		3365, 3260, 3151
$\nu_{C—H}$	2941	2940	2838	3025	
$\nu_{C=C/C=N}$	1595, 1493	1640, 1609	1629, 1602,	1587, 1530	
$\delta_{N—H}$			1575, 1546		1603, 1462
$\nu_{C=S}$					1401
$\nu_{C—N}$		1339, 1214,	1319, 1240,	1325, 1218,	1075
$\nu_{as\ (SO_3^-)}$	1169, 1093,	1171, 1104	1152, 1108		
$\nu_{s\ (SO_3^-)}$	1030, 998	1041, 1005	1032, 1004,		
$\delta_{C—H}$	846, 812,	821, 756	829, 681	852, 804,	
	705			733	
$Cd(NO_3)_2·4H_2O$, $Cd(Ac)_2·2H_2O$:					
$\nu_{as\ (NO_3^-)}$	1411, 1296				
$\nu_{(COO^-)}$	1525, 1438				

Table. S2 Selected bond lengths /Å and bond angles /° for complexes **1-4.**

complex 1			
Cd(1)-O(1)	2.4321(12)	S(1)-O(2)#2	1.4624(12)
Cd(1)-O(1)#1	2.4321(12)	S(1)-O(3)	1.4601 (12)
Cd(1)-O(2)	2.4141(12)	O(1)-Cd(1)-S(2) #1	80.96(3)
Cd(1)-O(2)#1	2.4141(12)	O(2)#1-Cd(1)-O(1)	85.25(4)
Cd(1)-S(2)	2.4988(4)	O(2)#1-Cd(1)-S(2) #1	89.92(3)
Cd(1)-S(2)#1	2.4988(4)	O(1)-S(1)-O(3)	111.48(7)
S(1)-O(1)	1.4591(12)	O(1)-S(1)-O(2)#1	112.66(7)
complex 2			
Cd(1)-O(1)	2.365(5)	O(6)-S(1)-O(5)	112.6(3)
Cd(1)-O(2)	2.482(5)	O(7)-S(1)-O(5)	111.0(3)
Cd(1)-O(3)	2.470(4)	O(7)-S(1)-O(6)	113.1(3)
Cd(1)-N(2)	2.397(5)	N(4)-Cd(1)-O(1)	90.31(18)
Cd(1)-N(4)	2.283(6)	N(4)-Cd(1)-O(2)	90.7(2)
Cd(1)-N(5)#1	2.283(6)	N(4)-Cd(1)-O(3)	87.52(17)
S(1)-O(5)	1.467(5)	N(4)-Cd(1)-O(5)	87.73(17)
S(1)-O(6)	1.451(5)	N(4)-Cd(1)-N(2)	94.5(2)
S(1)-O(7)	1.444(5)	N(5)#1-Cd(1)-O(1)	96.87(17)
O(1)-Cd(1)-O(2)	77.16(15)	N(5)#1-Cd(1)-O(2)	85.21(19)
O(1)-Cd(1)-N(2)	72.88(19)	N(5)#1-Cd(1)-O(3)	83.44(17)
O(3)-Cd(1)-O(2)	51.82(15)	N(5)#1-Cd(1)-O(5)	88.92(17)
O(5)-Cd(1)-O(3)	80.87(15)	N(5)#1-Cd(1)-N(2)	93.2(2)
O(5)-Cd(1)-N(2)	77.54(18)		
complex 3			
Cd(1)-O(1)	2.384(2)	O(5)-Cd(1)-O(3)	80.45(10)
Cd(1)-O(1)#1	2.385(2)	N(1)-Cd(1)-O(1)	94.91(9)
Cd(1)-O(2)	2.546(2)	N(1)-Cd(1)-O(1)#1	87.91(8)
Cd(1)-O(3)	2.350(2)	N(1)-Cd(1)-O(2)	90.74(9)
Cd(1)-O(5)	2.332(3)	N(1)-Cd(1)-O(3)	89.63(9)
Cd(1)-N(1)	2.318(2)	N(1)-Cd(1)-O(5)	92.97(9)
Cd(1)-N(2)	2.338(2)	N(2)-Cd(1)-O(1)	86.58(8)
S(1)-O(3)	1.460(2)	N(2)-Cd(1)-O(1)#1	89.09(8)
S(1)-O(4)	1.448(3)	N(2)-Cd(1)-O(2)	93.03(9)
S(1)-O(7)	1.454(3)	N(2)-Cd(1)-O(3)	87.37(9)
O(1)-Cd(1)-O(1)#1	72.53(9)	N(2)-Cd(1)-O(5)	89.03(9)
O(1)-Cd(1)-O(2)	52.14(8)	O(4)-S(1)-O(3)	111.55(16)
O(3)-Cd(1)-O(1)#1	80.07(8)	O(4)-S(1)-O(7)	114.26(17)
O(5)-Cd(1)-O(2)	75.18(10)	O(7)-S(1)-O(3)	112.19(16)

complex 4			
Cd(1)-O(7)	2.3257(18)	O(10)-Cd(1)-N(31)	89.48(7)
Cd(1)-O(8)	2.3132(17)	N(11)-Cd(1)- O(10)	87.17(6)
Cd(1)-O(10)	2.2844(18)	N(11)-Cd(1)- O(8)	98.45(6)
Cd(1)-N(11)	2.364(2)	N(11)-Cd(1)- O(7)	86.51(6)
Cd(1)-N(21)	2.360(2)	N(11)-Cd(1)- N(31)	87.65(7)
Cd(1)-N(31)	2.328(2)	N(21)-Cd(1)-O(10)	89.96(6)
S(1)-O(1)	1.4698(18)	N(21)-Cd(1)-O(8)	86.45(6)
S(1)-O(2)	1.4570(18)	N(21)-Cd(1)-O(7)	97.13(6)
S(1)-O(3)	1.4573(18)	N(21)-Cd(1)-N(31)	87.23(7)
O(7)-Cd(1)-N(31)	99.59(7)	O(2)-S(1)-O(3)	111.90(11)
O(8)-Cd(1)-O(7)	85.06(7)	O(2)-S(1)-O(1)	112.04(10)
O(10)-Cd(1)-O(8)	86.63(6)	O(3)-S(1)-O(1)	113.13(11)

Symmetry operation:
For **1**: #1 -x+1, -y+1, -z+1;
For **2**: #1 x+1, y, z;
For **3**: #1 -x+1, -y+1, -z+1.

Table. S3 hydrogen bond parameters for complexes **1-4.**

complex 1				
D-H···A	d(D···H)/Å	d(H···A)/Å	d(D···A)/Å	<(DHA)/º
N1-H1A...O3_#1	0.88	2.11	2.935(2)	155.7
N1-H1B...O3_#2	0.88	2.35	3.220(2)	172.2
N2-H2A...O3_#1	0.88	2.37	3.1312(19)	144.2
N2-H2B...O2_#3	0.88	2.13	2.9737(19)	159.8
complex 2				
C1-H18...O2	0.92(7)	2.35(6)	2.997(8)	127(5)
C2-H21B...O3_#1	1.10(9)	2.41(9)	3.452(10)	157(6)
C18-H37...O3	0.94(7)	2.56(7)	3.246(9)	131(5)
C21-H31...O6_#2	0.97(7)	2.56(7)	3.273(8)	130(5)
N2-H16A...O6	0.93(6)	1.82(6)	2.721(8)	161(5)
complex 3				
O5-H5A...O6_#1	0.86	1.86	2.711(4)	169.1
O5-H5B...O7	0.76	2.05	2.764(4)	156.6
O6-H6A...O2	0.76	2.17	2.924(4)	170.5
O6-H6B...O4_#2	0.76	1.99	2.694(4)	152.4
complex 4				
O7-H7A...O9	0.87	1.93	2.786(3)	169.1
O7-H7B...O3	0.87	2.05	2.828(2)	149.2
O8-H8A...O2_#1	0.87	1.90	2.726(2)	156.4
O8-H8B...O1	0.87	1.96	2.768(2)	154.5
O9-H9A...O1_#1	0.87	2.03	2.896(3)	178.9
O9-H9B...O3_#2	0.87	2.22	3.051(3)	160.7

O10-H10A...N41_#3	0.87	1.96	2.794(3)	160.1
O10-H10B...N51_#4	0.87	1.95	2.795(3)	163.1

Symmetry operation:

For **1**, #1 -x+2, -y+2, -z+1; #2 -x+1, -y+2, -z+1; #3 -x+1, -y+1, -z+1.

For **2**, #1 -x+3/2, y-1/2, -z+3/2; #2 x-1/2, -y+1/2, z+1/2.

For **3**, #1 -x+1,-y,-z+1; #2 x+1/2,-y+1/2,z+1/2.

For **4**, #1-x+1,-y+1,-z+1; #2 -x,-y+1,-z+1; #3 x+1,y,z; #4 -x+1,y-1/2,-z+1/2.